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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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PROGRAMS FOR COMPUTING EQUILIBRIUM THERMODYNAMIC

PROPERTIES OF GASES

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SUMMARY

This report presents a series of subroutines, written in FORTRAN IV, for calculating the equilibrium thermodynamic properties of any mixture of reacting diatomic gases if the temperature, density, and molar concentrations of the species are given. One triatomic gas, carbon dioxide, may also be included in the mixture. Two additional subroutines permit the calculation of the molar concentrations of the species if the gas mixture is air. A sample main program is included which uses all these subroutines to compute the equilibrium composition and thermodynamic properties of air for a given density over a range of temperatures.

INTRODUCTION

Solutions to problems involving the flow of a chemically reacting gas require the computation of the equilibrium thermodynamic properties of the gas mixtures over wide ranges of temperature and density. These properties are available in tabular form for air (refs. 1, 2, and 3), in graphical form for carbon dioxide (ref. 4), and for three nitrogen carbon dioxide mixtures (ref. 5). However, neither the tabular nor graphical form is convenient for use in electronic machine calculations without elaborate and tedious curve fitting of the data. Therefore, the subroutines presented here should prove useful for the solution of many problems in the flow of a chemically reacting gas.

Five different subroutines are presented in this report. In addition, a main program designed to compute the equilibrium thermodynamic properties of air is presented to illustrate the use of the five subroutines. Two of the subroutines, SPECIE and ENTH, can be used to obtain the pressure, enthalpy, specific heat at constant pressure (with frozen composition), entropy, gas constant, and equilibrium constants of the components of a gas mixture. The various chemical and physical constants needed as input by subroutine SPECIE may be obtained from references 6 and 7. A third subroutine, RATCON, gives the reaction rates for eight chemical reactions in air. This subroutine would require modification if some other gas mixture were used. Two additional subroutines, GUESS and ITERA, calculate the equilibrium molar concentrations of each species for air at a given temperature and density. Although these subroutines would require major modification for any mixture other than air, they do provide a suitable basis from which similar programs for other mixtures could be written easily.

Each individual species is assumed to behave as an ideal gas. The thermodynamic properties of the diatomic species are approximated by the harmonic-oscillator rigid-rotator model with rotational and vibrational constants appropriate to the lowest electronic state. Computational results are given for two air models. Model A contains the species N_2 , O_2 , N , O , NO , NO^+ , O^+ , N^+ , and e^- . Model B contains the same nine species as model A plus two additional species, O^{++} and N^{++} .

SYMBOLS

c_p	specific heat at constant pressure (with composition frozen)
c_{p_i}	specific heat at constant pressure for the i th species
E_n	energy of the n th energy level
F_i	free energy of the i th species
g_n	degeneracy of the n th energy level
H	total enthalpy of the mixture
H_i	enthalpy of the i th species
H_{O_i}	enthalpy of formation of the i th species
K_i	equilibrium constant for the i th reaction
M_i	molecular weight of the i th species
n_i	number of atoms in the i th species
P	total pressure of the mixture
P_0	standard pressure of one atmosphere
p_i	partial pressure of the i th species
R	universal gas constant
S	total entropy of the mixture
S_i	entropy of the i th species
T	temperature, $^{\circ}K$
T_r	characteristic rotational temperature
T_v	characteristic vibrational temperature

ZN mass concentration of nitrogen atoms in cold mixture
 ZO mass concentration of oxygen atoms in cold mixture
 β_i sum of β_{ij} values over the index j
 β_{ij} difference of the stoichiometric coefficients of the j th species in the i th reaction
 γ_i concentration of the i th species in moles/gm

SAMPLE MAIN PROGRAM

This is a typical program (see appendix A) which uses all the following subroutines to compute the thermodynamic properties of equilibrium air. It is intended as a guide for the use of the subroutines SPECIES, ENTH, RATCON, GUESS, and ITERA. It by no means exhausts the possibilities for their use.

The sample program requires an input ΔT (DELTA), a density (RHO), and nine species concentrations for the cold mixture of nitrogen and oxygen (G(N)). The program will then call the appropriate subroutines for the computation of the thermodynamic properties pressure, gas constant, enthalpy, entropy, specific heat at constant pressure, equilibrium constants, reaction rate constants (as defined under subroutine RATCON), and the species concentrations. These computations will be performed at the given density for 25 temperatures starting at ΔT and ending at $25 \Delta T$. A sample output is given for air at a density of 0.01288 gm/cm^3 and at 4 temperatures from 1000° K to 4000° K .

SUBROUTINE SPECIE

This subroutine (see appendix B) will compute the pressure (P),¹ enthalpy (H(21)), specific heat at constant pressure (with composition frozen) (CP(21)), entropy (FE(21)), equilibrium constants (BK(J)), reaction rate constants (AK(J)), and the gas constant (GCONST) for a given temperature (T), density (R), and the molar concentrations (GA(J)) of each species. On the first entry to the subroutine, all necessary chemical and physical constants are read from cards and stored in the program. Provision has been made for the computation of 20 species and 40 reactions.

This subroutine uses the following equations to compute the thermodynamic properties of the mixture from the thermodynamic properties of the components.

¹Characters in parentheses are those used in the FORTRAN listing in the appendixes. There is an unavoidable inconsistency between these characters and those defined under Symbols.

The enthalpy is given by

$$\frac{H}{RT} = \sum \gamma_i \frac{H_i}{RT} \quad (1)$$

The specific heat at constant pressure (with frozen composition) is given by

$$c_p = \sum \gamma_i c_{p_i} \quad (2)$$

The entropy of the mixture is given by

$$\frac{S}{R} = \sum \gamma_i \left[\frac{H_i}{RT} - \frac{F_i}{RT} - \ln \frac{p_i}{P_0} \right] \quad (3)$$

The total pressure of the mixture is

$$P = \rho RT \sum \gamma_i \quad (4)$$

The equilibrium constant for each reaction is

$$\ln K_i = - \sum \beta_{ij} \frac{F_j}{RT} - \beta_i \ln(82.055761 T) \quad (5)$$

The partial pressure of each species is computed from

$$p_i = \frac{\gamma_i}{\sum \gamma_i} P \quad (6)$$

The entropy of each species is computed in this subroutine as

$$S_i = H_i - F_i \quad (7)$$

The data that must be input to this subroutine are the number of reactions (IL), the number of species (JL), the stoichiometric coefficients for each reaction (B(I,J)), the number of electronic energy levels for each species (NL(J)), the energy (E(J,N)) and degeneracy (G(J,N)) of each of these electronic energy levels, the number of atoms in each molecule (ENJ(J)), the vibrational (TV(J)) and rotational (TR) temperatures of each diatomic species, the heat of formation (ENTH(J)) of each species, the molecular weight (EMWT(J)) of each species, and finally the percent by volume (GX(J)) of each species in the cold mixture. All this information is stored in the subroutine and used on all subsequent entries for the computation of the thermodynamic properties.

Each time the subroutine is called it must be given the temperature (T), in degrees Kelvin, the density (R) in gm/cm³, and the mass concentrations (GA(I)), in moles/gm. The subroutine will then compute all the quantities

listed in the first paragraph of this section. In addition, the enthalpy (H(J)), entropy (FE(J)), and specific heat at constant pressure (CP(J)) for each individual species (J = 1, JL) will be computed.

Subroutine SPECIE uses two subroutines, ENTH and RATCON, which are discussed in subsequent sections.

Sample input data required by subroutine SPECIE are shown in appendix F. The input data are shown for model A and model B.

SUBROUTINE ENTH

This subroutine (see appendix C) will compute the enthalpy (H), specific heat at constant pressure (CP), and free energy (FE) of a given species for a given temperature (TX). For each species, this subroutine must be given the heat of formation (ENTAX), the number of atoms in one molecule of the species (ENJX), the vibrational temperature (TVX), the number of electronic states (NLX), as well as the energy (EX) and degeneracy (GX) of each electronic state and a constant (EMWTX) which depends on the molecular weight of the species and the rotational temperature of the species.

The computations performed by this subroutine are based on the harmonic-oscillator rigid-rotator model for all diatomic molecules. It is also possible to compute the thermodynamic functions for one triatomic molecule, carbon dioxide. In this computation it is assumed that there is only a ground electronic state for the carbon dioxide molecules.

The equations used by this subroutine for the computation of the thermodynamic functions of each individual species are as follows. The free energy is computed from

$$\begin{aligned} \frac{F_i}{RT} = & -\ln \sum g_n e^{-E_n/T} - [(n_i - 1) + 2.5] \ln T - 1.5 \ln M_i + 3.6649516 \\ & + (n_i - 1) \ln \left(1 - e^{-T_v/T} \right) + (n_i - 1) \ln T_r + \frac{H_{o,i}}{RT} \end{aligned} \quad (8)$$

The enthalpy of each species is

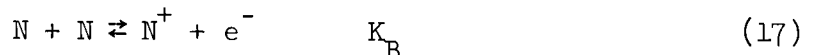
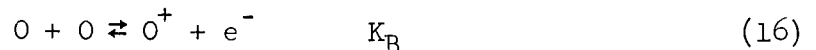
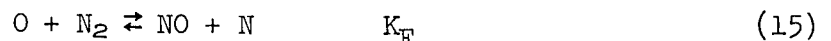
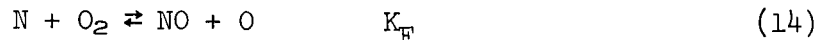
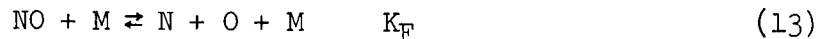
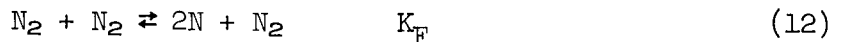
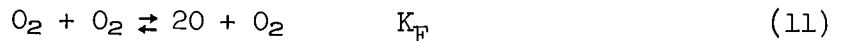
$$\frac{H_i}{RT} = [(n_i - 1) + 2.5] + \frac{1}{T} \frac{\sum g_n E_n e^{-E_n/T}}{\sum g_n e^{-E_n/T}} + \frac{(n_i - 1) T_v}{T(e^{T_v/T} - 1)} + \frac{H_{o,i}}{RT} \quad (9)$$

The specific heat at constant pressure (with frozen composition) is

$$c_{p_i} = [(n_i - 1) + 2.5] + (n_i - 1) \left(\frac{T_v}{T} \right)^2 \frac{e^{T_v/T}}{(e^{T_v/T} - 1)^2} + \frac{1}{T^2} \frac{\left(\sum g_n e^{-E_n/T} \right) \left(\sum g_n E_n^2 e^{-E_n/T} \right) - \left(\sum g_n E_n e^{-E_n/T} \right)^2}{\left(\sum g_n e^{-E_n/T} \right)^2} \quad (10)$$

SUBROUTINE RATCON

This subroutine (see appendix D) will compute the rate constants for a given temperature according to the formulas and constants of references 8 and 9 for the reactions listed below.



The symbol K_F after a reaction indicates the forward rate constant; K_B indicates the backward rate constant.

This routine requires only the temperature as input. It is a simple matter to alter this subroutine to give the rate constants for any reaction desired.

SUBROUTINES GUESS AND ITERA

For any mixture of nitrogen and oxygen, two additional subroutines (see appendix E) are available that permit the computation of the equilibrium species concentrations at a given temperature and density. These two

subroutines require as input the temperature (T), the density (RHO), the atom concentrations of the cold mixture (ZN,ZO), and eight equilibrium constants (EK(I)).

The first subroutine GUESS estimates the relative magnitude of the various species concentrations. The second subroutine ITERA then refines these guessed values until they satisfy the three conservation equations, that is, conservation of oxygen atoms, nitrogen atoms, and charge, as well as six equilibrium equations. These two subroutines require a block of common storage called /COM4/ which contains arrays for 20 equilibrium constants (EK(20)), 20 mass concentrations (B(20)), 20 first guesses (C(20)) of the mass concentrations, the density (RHO), and the cold mass concentrations of nitrogen atoms (ZN) and oxygen atoms (ZO).

The equations that must be solved by subroutine ITERA are listed below.

$$ZO = \gamma_O + 2\gamma_{O_2} + \gamma_{NO} + \gamma_{NO^+} + \gamma_{O^+} \quad (19)$$

$$ZN = \gamma_N + 2\gamma_{N_2} + \gamma_{NO} + \gamma_{NO^+} + \gamma_{N^+} \quad (20)$$

$$\gamma_{e^-} = \gamma_{NO^+} + \gamma_{O^+} + \gamma_{N^+} \quad (21)$$

$$K_1 = \frac{\rho \gamma_O^2}{\gamma_{O_2}} \quad (22)$$

$$K_2 = \frac{\rho \gamma_N^2}{\gamma_{N_2}} \quad (23)$$

$$K_3 = \frac{\rho \gamma_O \gamma_N}{\gamma_{NO}} \quad (24)$$

$$K_6 = \frac{\rho \gamma_{e^-} \gamma_{O^+}}{\gamma_O} \quad (25)$$

$$K_7 = \frac{\rho \gamma_{e^-} \gamma_{N^+}}{\gamma_N} \quad (26)$$

$$K_8 = \frac{\gamma_{e^-} \gamma_{NO^+}}{\gamma_O \gamma_N} \quad (27)$$

The convergence of the iteration process used in subroutine ITERA requires that equation (19) be solved for the largest of γ_O , γ_{O_2} , or γ_{O^+} , and that equation (20) be solved for the largest of γ_N , γ_{N_2} , or γ_{N^+} . The remaining γ_i values are then found from equations (22) through (27). The value of γ_{e^-} is always found from equation (21). The path taken in subroutine

ITERA depends therefore on the relative magnitudes of γ_O , γ_{O_2} , γ_{O^+} and of γ_N , γ_{N_2} , and γ_{N^+} . The function of subroutine GUESS is to provide an initial guess of these relative magnitudes. This initial guess is based on the temperature and density of the mixture and on the relative values of the equilibrium constants K_1 and K_6 for oxygen and K_2 and K_7 for nitrogen.

Based on these guessed values, subroutine ITERA then computes the species concentrations by iterating equations (19) through (27) until all the equations are satisfied. At each step in the iteration the newest value of each concentration is computed as the average between the value obtained on the previous iteration and the value computed on the present iteration. The iteration is terminated when the change in the values for two successive iterations is less than a specified amount (10^{-7} for model A and 10^{-5} for model B) and when all the equations are satisfied to within a specified amount (5×10^{-8} for model A and 10^{-6} for model B).

Appendix E gives two listings for subroutine ITERA and two listings for subroutine GUESS. In each case one listing is for model A (contains no O^{++} or N^{++}) and one listing is for model B (contains O^{++} and N^{++}).

POSSIBLE USES OF THE PROGRAMS

A series of programs for computing the thermodynamic properties of a variety of gases is presented. In addition, two of the programs permit the computation of the equilibrium species concentrations of air or any other mixture of nitrogen and oxygen, as well as the thermodynamic properties of the mixture.

The programs are presented in a form which can be modified easily to suit the user's needs. For instance, the thermodynamic properties of any diatomic or monatomic gas may be obtained simply by altering the input data to subroutine SPECIE. Subroutine RATCON can be easily altered to give any rate constant desired. Subroutines GUESS and ITERA may be rewritten to give the equilibrium concentrations of gas mixtures other than air. All the subroutines as presented may be used in a new main program to compute the equilibrium flow properties behind a normal shock wave.

DISCUSSION OF RESULTS

The main program described in this report has been used to compute the thermodynamic properties of air. Two different models have been used. In model A the species assumed to be present are N_2 , O_2 , NO , N , O , NO^+ , N^+ , O^+ , and e^- . Model B contains N^{++} and O^{++} in addition to the species in model A. The values obtained are compared to the values presented in references 2 and 3 (table I) and to the values presented in reference 1 (table II).

The dimensionless enthalpy, H/RT , computed for model A agrees with the values presented in reference 2 to within 1 percent except at $15,000^{\circ}\text{K}$, where the error rises to 1.39 percent at 100 times standard density and to 8.46 percent at 10^{-7} times standard density. The dimensionless entropy, S/R , computed for model A, agrees with that computed in reference 2 to within 0.5 percent except at $15,000^{\circ}\text{K}$ and 10^{-7} times standard density where the error is 2.54 percent. The pressure (in atmospheres), for model A, agrees with that computed in reference 2 to within 3 percent except at $15,000^{\circ}\text{K}$ and 10^{-7} times standard density where the error is 3.27 percent.

The increase in error at $15,000^{\circ}\text{K}$ for enthalpy, entropy, and pressure is attributed to inadequacies in model A. The neglect of species N^{++} and O^{++} begins to be felt at $15,000^{\circ}\text{K}$. That this is indeed the case may be seen by comparing the results computed for model B to the results of reference 2. At $15,000^{\circ}\text{K}$ and $\rho/\rho_0 = 10^{-7}$, the error in the dimensionless enthalpy drops from 8.46 to 0.13 percent, the error in dimensionless entropy drops from 2.54 to 0.25 percent, and the error in pressure drops from 3.27 to 0.28 percent.

The highest temperature available in references 2 and 3 is $15,000^{\circ}\text{K}$. Therefore, for comparisons at higher temperatures, it is necessary to use the results of reference 1. The comparison between values in reference 1 and the present calculations is presented in table II. Again, comparison is made with both the model A and model B air of the present report. At $18,000^{\circ}\text{K}$ and $25,000^{\circ}\text{K}$ and at $\rho/\rho_0 = 10^{-6}$, the errors in model A are seen to be enormous. However, for model B, which includes N^{++} and O^{++} , the errors at these points are drastically reduced. In fact, they become comparable to the errors in the low temperature region.

CONCLUSIONS

A series of subroutines written in FORTRAN IV is presented. These programs may be used to compute the thermodynamic properties at a given density and temperature of any diatomic gas plus the one triatomic gas, CO_2 , if the molar concentrations are given. In the special case of air, additional subroutines are included that permit the computation of the molar concentrations themselves. The thermodynamic properties of two models for air are compared to the results obtained by other investigators.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., Dec. 28, 1966
129-01-08-20

APPENDIX A

```

$IBFTC MAIN      NCREF
CMAIN CHECKOUT  BAILEY
COMMON/COM4/EK(20),B(20),C(20),RHO,ZN,ZO
DIMENSION AK(20),BK(20),H(21),CP(21),S(21),G(21)
READ(5,12) NMAX
12  FORMAT(13)
    READ(5,2) DELTA
2   FORMAT(F15.6)
    READ(5,4) (G(N),N=1,9)
4   FORMAT(5F15.6)
    ZN=2.*G(5)
    ZC=2.*G(4)
1   READ(5,2) RHC
    TEMP=0.
    WRITE(6,13)
13  FORMAT(12H1TEMPERATURE/79H DENSITY,PRESSURE,GAS CONSTANT,ENTHALPY,
1ENTROPY,CONSTANT PRESSURE SPECIFIC HEAT/9H ENTHALPY/8H ENTROPY/32H
2 CONSTANT PRESSURE SPECIFIC HEAT/21H EQUILIBRIUM CONSTANT/14H REAC
3TION RATE/19H MASS CONCENTRATION/34H O,N,E-,O2,N2,NO,NO+,O+,N+,O++
4,N++)
    DO 3 M=1,NMAX
        TEMP=TEMP+DELTA
        CALL SPECIE(TEMP,RHO,PRESS,G,H,CP,S,AK,BK,GCONST)
        DO 8 N=1,11
            IF(BK(N)-82.) 9,9,10
9         EK(N)=10.**BK(N)
            GO TO 8
10        EK(N)=1.E+36
8         CONTINUE
        CALL GUESS
        CALL ITERA
        DO 11 N=1,11
11        G(N)=B(N)
        CALL SPECIE(TEMP,RHO,PRESS,G,H,CP,S,AK,BK,GCONST)
        WRITE(6,5) TEMP,RHO,PRESS,GCONST,H(21),S(21),CP(21)
5        FORMAT(1H0,E15.6/10X,6E15.6)
        WRITE(6,6) (H(N),N=1,11)
        WRITE(6,6) (S(N),N=1,11)
        WRITE(6,6) (CP(N),N=1,11)
        WRITE(6,6) (BK(N),N=1,10)
        WRITE(6,6) (AK(N),N=1,10)
        WRITE(6,6) (G(N),N=1,11)
6        FORMAT(1H ,11E11.4)
3        CONTINUE
        WRITE(6,7)
7        FORMAT(1H0,10HEND OF RUN)
        GO TO 1
    END

```


APPENDIX B

```

91BFTC TC1209 NOREF
SUBROUTINE SPECIE(T,R,P,GA,H,CP,FE,AK,BK,GCONST)
DIMENSION G(20,10),E(20,10),ENJ(20),TV(20),ENTAI(20),EMWT(20)
DIMENSION EMPX(20),NL(20),BT(40),B(40,20),EX(20),GX(20)
DIMENSION GA(2),AK(2),BK(2),CP(2),H(2),FE(2)
IF(AT7-7) 2,3,2
2 NT7=1
D=.43429448
READ(5,4) IL,JL
FORMAT(2I3)
4 DC 5 I=1,IL
5 REAC(5,6) (B(I,J),J=1,JL)
6 FORMAT(20F6.1)
DC 7 I=1,IL
BT(I)=0.
DO 7 J=1,JL
BT(I)=BT(I)+B(I,J)
DO 8 J=1,JL
REAC(5,4) NL(J)
NL=NL(J)
DC 9 N=1,NLL
REAC(5,10) G(J,N),E(J,N)
FORMAT(5F15.6)
10 E(J,N)=1.4587886+E(J,N)
5 REAC(5,10) ENJ(J),TV(J),ENTA(J),EMWT(J),TR
EMX(J)=EMWT(J)
ENTA(J)=ENTA(J)/1.98647
IF(ENJ(J)-2.5) 16,16,17
17 EMWT(J)=1.5*ALOG(EMWT(J))-3.6645516-ALOG(TR)
GO TO 8
16 EMWT(J)=1.5*ALOG(EMWT(J))-3.6645516-(ENJ(J)-1.)*ALOG(TR)
8 CONTINUE
REAC(5,10) (GX(N),N=1,JL)
CMWT=0.
DC 19 N=1,JL
CMWT=CMWT+GX(N)*EMX(N)
19 TST0=273.15
PSTD=1.01325E+06
3 TX=T
RX=R
GA(21)=0.
DC 1 N=1,JL
GA(21)=GA(21)+GA(N)
1 GCONST=8.3143E+07*GA(21)
PX=RX*TX*GCONST
P=PX

```

APPENDIX C

```

$IBFTC TC1210 NOREF
SUBROUTINE ENTH(TX,ENTAX,ENJX,TVX,EMWTX,EX,GX,NLX,H,CP,FE)
DIMENSION EX(20),GX(20)
NX=IFIX(ENJX)
GO TO(1,2,3),NX
1  SUM1=0.
   SUM2=0.
   SUM3=0.
   DO 4 N=1,NLX
     XX=GX(N)*EXP(-EX(N)/TX)
     SUM1=SUM1+XX
     SUM2=SUM2+XX*EX(N)
4  SUM3=SUM3+EX(N)*EX(N)*XX
   FE=-ALOG(SUM1)-2.5*ALOG(TX)-EMWTX+ENTAX/TX
   H=2.5+SUM2/(TX*SUM1)+ENTAX/TX
   CP=2.5+(SUM1*SUM3-SUM2**2)/((TX*SUM1)**2)
   GO TO 5
2  SUM1=0.
   SUM2=0.
   SUM3=0.
   DO 6 N=1,NLX
     XX=GX(N)*EXP(-EX(N)/TX)
     SUM1=SUM1+XX
     SUM2=SUM2+XX*EX(N)
6  SUM3=SUM3+EX(N)*EX(N)*XX
   FE=-ALOG(SUM1)-3.5*ALOG(TX)-EMWTX+ENTAX/TX
   H=3.5+SUM2/(TX*SUM1)+ENTAX/TX
   CP=3.5+(SUM1*SUM3-SUM2**2)/((TX*SUM1)**2)
   IF(TVX/TX-88.0) 7,7,8
8  VIBH=0.
   VIBCP=0.
   R2=0.
   GO TO 9
7  A1=EXP(TVX/TX)
   R2=ALOG(1.-EXP(-TVX/TX))
   A11=A1-1.
   VIBH=(TVX/TX)/A11
   VIBCP=(TVX/TX)**2
   VIBCP=(VIBCP/A11)*(A1/A11)
9  CP=CP+VIBCP
   H=H+VIBH
   FE=FE+R2
   GO TO 5
3  VIB1=1932.1/TX
   VIB2=960.1/TX
   VIB3=3380./TX
   VIB11=1./(1.-EXP(-VIB1))
   VIB22=1./(1.-EXP(-VIB2))
   VIB33=1./(1.-EXP(-VIB3))
   VIB1C=VIB1**2*EXP(VIB1)/(EXP(VIB1)-1.)**2
   VIB2C=VIB2**2*EXP(VIB2)/(EXP(VIB2)-1.)**2
   VIB3C=VIB3**2*EXP(VIB3)/(EXP(VIB3)-1.)**2
   VIB1=VIB1/(EXP(VIB1)-1.)
   VIB2=VIB2/(EXP(VIB2)-1.)
   VIB3=VIB3/(EXP(VIB3)-1.)
   H=3.5+VIB1+2.*VIB2+VIB3+ENTAX/TX
   FE=-3.5*ALOG(TX)-ALOG(VIB11*VIB22*VIB33)-EMWTX+ENTAX/TX
   CP=3.5+VIB1C+2.*VIB2C+VIB3C
5  RETURN
END

```

APPENDIX D

```
$IBFTC TC1208 . Noref
SUBROUTINE RATCON(AK,TX)
DIMENSION AK(10)
T15=TX*SQRT(TX)
AK(1)=3.6E+21*EXP(-59380./TX)/T15
AK(2)=1.5E+20/T15
AK(3)=5.18E+21*EXP(-75490./TX)/T15
AK(4)=1.0E+12*EXP(-3120./TX)*SQRT(TX)
AK(5)=5.0E+13*EXP(-38016./TX)
AK(6)=6.0E+24/(T15*TX)
AK(7)=AK(6)
AK(8)=1.8E+21/T15
RETURN
END
```


APPENDIX E

MODEL A

```

$1BFTC TC1207 NOREF
SUBROUTINE GUESS
COMMON/COM4/EK(20),B(20),C(20),RHO,ZN,ZO
C1=.5*EK(11)/RHO
IF(C1-100.) 9,9,10
9 B(1)=-C1+SQRT(C1*C1+4.*C1*ZO)
GO TO 6
10 B(1)=2.*ZO*(1.-ZC/C1)
6 B(1)=B(1)/2.
B(4)=(ZO-B(1))/2.
IF(B(4)) 1,1,2
1 B(4)=0.
2 C2=.5*EK(2)/RHO
IF(C2-100.) 11,11,12
11 B(2)=-C2+SQRT(C2*C2+4.*C2*ZN)
GO TO 8
12 B(2)=2.*ZN*(1.-ZN/C2)
8 B(2)=B(2)/2.
B(5)=(ZN-B(2))/2.
IF(B(5)) 3,3,4
3 B(5)=0.
4 B(6)=B(1)*B(2)*RHO/EK(3)
B(3)=SQRT(B(1)*B(2)*EK(8))
B3=SQRT(B(2)*EK(7)/RHO)
IF(B3-B(3)) 5,5,7
7 ZQO=.9*ZN
B(3)=AMIN1(B3,ZQO)
B(8)=-.25*B(3)
B(9)=-.75*B(3)
GO TO 13
5 B(7)=B(3)
13 RETURN
END

```

MODEL B

```

$1BFTC GUESS NOREF
SUBROUTINE GUESS
COMMON/COM4/EK(20),B(20),C(20),RHO,ZN,ZO
C1=.5*EK(11)/RHO
IF(C1-100.) 9,9,10
9 B(1)=-C1+SQRT(C1*C1+4.*C1*ZO)
GO TO 6
10 B(1)=2.*ZO*(1.-ZC/C1)
6 B(1)=B(1)/2.
B(4)=(ZO-B(1))/2.
IF(B(4)) 1,1,2
1 B(4)=0.
2 C2=.5*EK(2)/RHO
IF(C2-100.) 11,11,12
11 B(2)=-C2+SQRT(C2*C2+4.*C2*ZN)
GO TO 8
12 B(2)=2.*ZN*(1.-ZN/C2)
8 B(2)=B(2)/2.
B(5)=(ZN-B(2))/2.
IF(B(5)) 3,3,4
3 B(5)=0.
4 B(6)=B(1)*B(2)*RHO/EK(3)
B(3)=SQRT(B(1)*B(2)*EK(8))
B3=SQRT(B(2)*EK(7)/RHO)
IF(B3-B(3)) 5,5,7
7 ZQO=.9*ZN
B(3)=AMIN1(B3,ZQO)
B(4)=0.
B(5)=0.
B(11)=0.
B(2)=0.
IF(EK(10)/(B(3)*RHO)-1.) 14,14,15
15 B(11)=-.75*B(3)
B(9)=-.25*B(11)
GO TO 16
14 B(9)=-.75*B(3)
B(11)=-.25*B(9)
16 IF(EK(9)/(B(3)*RHO)-1.) 17,17,18
18 B(10)=-.25*B(3)
B(8)=-.25*B(10)
GO TO 13
17 B(8)=-.25*B(3)
B(10)=-.25*B(8)
GO TO 13
5 B(7)=B(3)
B(8)=0.
B(9)=B(8)
B(10)=B(9)
B(11)=B(10)
13 RETURN
END

```

```

$IBFTC TC1206 NCREF
SUBROUTINE ITERA
COMMON/COM4/EK(20),B(20),C(20),RHO,ZN,ZO
DATA DEL1,DEL2/1.E-07,5.E-08/
DO 9 N=1,200
  IF(B(4)-B(1)) 1,1,2
2  C(4)=(ZC-B(1)-B(6)-B(7)-B(8))/2.
  B(4)=(B(4)+C(4))/2.
  C(1)=SQRT(B(4)*EK(1)/RHO)
  B(1)=(B(1)+C(1))/2.
  C(8)=(B(1)/B(3))*(EK(6)/RHO)
  B(8)=(B(8)+C(8))/2.
  NTEST1=1
  GO TO 3
1  IF(B(1)-B(8)) 4,4,5
5  C(1)=ZC-2.*B(4)-B(6)-B(7)-B(8)
  B(1)=(B(1)+C(1))/2.
  C(4)=RHO*B(1)*B(1)/EK(1)
  B(4)=(B(4)+C(4))/2.
  C(8)=(B(1)/B(3))*(EK(6)/RHO)
  B(8)=(B(8)+C(8))/2.
  NTEST1=2
  GO TO 3
4  C(8)=ZC-B(1)-2.*B(4)-B(6)-B(7)
  B(8)=(B(8)+C(8))/2.
  C(1)=RHO*B(3)*B(8)/EK(6)
  B(1)=(B(1)+C(1))/2.
  C(4)=RHO*B(1)*B(1)/EK(1)
  B(4)=(B(4)+C(4))/2.
  NTEST1=3
3  IF(B(5)-B(2)) 6,6,7
7  C(5)=(ZN-B(2)-B(6)-B(7)-B(9))/2.
  B(5)=(B(5)+C(5))/2.
  C(2)=SQRT(B(5)*EK(2)/RHO)
  B(2)=(B(2)+C(2))/2.
  C(9)=(B(2)/B(3))*(EK(7)/RHO)
  B(9)=(B(9)+C(9))/2.
  NTEST2=1
  GO TO 8
6  IF(B(2)-B(9)) 31,31,32
32 C(2)=ZN-2.*B(5)-B(6)-B(7)-B(9)
  B(2)=(B(2)+C(2))/2.
  C(5)=RHO*B(2)*B(2)/EK(2)
  B(5)=(B(5)+C(5))/2.
  C(9)=(B(2)/B(3))*(EK(7)/RHO)
  B(9)=(B(9)+C(9))/2.

  NTEST2=2
  GO TO 8
31 C(9)=ZN-B(2)-2.*B(5)-B(6)-B(7)
  B(9)=(B(9)+C(9))/2.
  C(2)=RHO*B(3)*B(9)/EK(7)
  B(2)=(B(2)+C(2))/2.
  C(5)=RHO*B(2)*B(2)/EK(2)
  B(5)=(B(5)+C(5))/2.
  NTEST2=3
8  C(3)=B(7)+B(8)+B(9)
  B(3)=(B(3)+C(3))/2.
  C(6)=RHO*B(1)*B(2)/EK(3)
  B(6)=(B(6)+C(6))/2.
  C(7)=B(1)*B(2)*EK(8)/B(3)
  B(7)=(B(7)+C(7))/2.
10 IF(ABS((C(1)-B(1))/B(1))-DEL1) 11,11,9
11 IF(ABS((C(2)-B(2))/B(2))-DEL1) 12,12,9
12 IF(ABS((C(3)-B(3))/B(3))-DEL1) 13,13,9
13 IF(ABS((C(4)-B(4))/B(4))-DEL1) 14,14,9
14 IF(ABS((C(5)-B(5))/B(5))-DEL1) 15,15,9
15 IF(ABS((C(6)-B(6))/B(6))-DEL1) 16,16,9
16 IF(ABS((C(7)-B(7))/B(7))-DEL1) 17,17,9
17 IF(ABS((C(8)-B(8))/B(8))-DEL1) 18,18,9
18 IF(ABS((C(9)-B(9))/B(9))-DEL1) 19,19,9
19 D1=ZC-B(1)-2.*B(4)-B(6)-B(7)-B(8)
  D2=ZN-B(2)-2.*B(5)-B(6)-B(7)-B(9)
  D3=B(3)-B(7)-B(8)-B(9)
  D4=B(4)*EK(1)-RHO*B(1)*B(1)
  D5=B(5)*EK(2)-RHO*B(2)*B(2)
  D6=B(6)*EK(3)-RHO*B(1)*B(2)
  D7=B(1)*EK(6)-RHO*B(3)*B(8)
  D8=B(2)*EK(7)-RHO*B(3)*B(9)
  D9=B(1)*B(2)*EK(8)-B(3)*B(7)
  IF(ABS(D1)-DEL2) 22,22,9
22 IF(ABS(D2)-DEL2) 23,23,9
23 IF(ABS(D3)-DEL2) 24,24,9
24 IF(ABS(D4)-DEL2) 25,25,9
25 IF(ABS(D5)-DEL2) 26,26,9
26 IF(ABS(D6)-DEL2) 27,27,9
27 IF(ABS(D7)-DEL2) 28,28,9
28 IF(ABS(D8)-DEL2) 29,29,9
29 IF(ABS(D9)-DEL2) 30,30,9
30 GO TO 33
9  CONTINUE
  WRITE(6,34)NTEST1,NTEST2,(B(J),J=1,9)
34 FORMAT(1H0,22HNO CONVERGENCE NTEST1=13,
7HNTTEST2=13/1H,1P9E14.6)
  CALL EXIT
33 RETURN
  END

```


010011		MODEL B					
2.	-1.	-1.	-1.				
1.	1.		-1.				
1.	-1.	-1.	1.				
-1.	1.	-1.	1.				
-1.	1.			1.			
-1.	-1.	1.		1.			
-1.	-1.	1.		-1.0	1.0		
	1.0			-1.0	1.0		
	1.0				1.0		
5	1	0.0		OXYGEN ATCM			
5.0		159.0		OXYGEN ATCM			
3.0		227.0		OXYGEN ATCM			
1.0		15868.0		OXYGEN ATCM			
5.0		33792.0		OXYGEN ATCM			
1.0		0.0	58980.0	OXYGEN ATOM	16.000	1.0	0
1.0				NITROGEN ATOM			
5	2	0.0		NITROGEN ATOM			
4.0		19228.0		NITROGEN ATOM			
6.0		19281.0		NITROGEN ATOM			
4.0		28840.0		NITROGEN ATOM			
4.0		28840.0		NITROGEN ATOM			
2.0		0.0	112590.0	NITROGEN ATOM	14.007	1.0	N
1.0							
1	3	NL ANC J	ELECTRON	G AND E ELECTRON			
2.0		0.0		.0C054847	1.0		E-
1.		0.0	0.0	OXYGEN MOLECULE			
5	4	0.0		OXYGEN MOLECULE			
3.0		7918.0		OXYGEN MOLECULE			
2.0		13195.0		OXYGEN MOLECULE			
1.0		36096.0		OXYGEN MOLECULE			
3.0		49802.0		OXYGEN MOLECULE			
3.0		2256.0	0.0	OXYGEN MOLECULE	32.000	4.160	O2
2.0				NITROGEN MOLECULE			
4	5	0.0		NITROGEN MOLECULE			
1.0		50256.0		NITROGEN MOLECULE			
3.0		59626.0		NITROGEN MOLECULE			
6.0		60000.0		NITROGEN MOLECULE			
1.0		3374.0	0.0	NITROGEN MOLECULE			
2.0				28.014	5.784		N2
4	6	0.0		NITRIC OXIDE			
2.0		121.0		NITRIC OXIDE			
2.0		43966.0		NITRIC OXIDE			
2.0		45918.0		NITRIC OXIDE			
4.0		2719.0	21477.0	NITRIC OXIDE			
2.0				30.007	2.453		NO
4	7	0.0		NITRIC OXIDE ION			
1.0		20000.0		NITRIC OXIDE ION			
3.0		31000.0		NITRIC OXIDE ION			
6.0		36000.0		NITRIC OXIDE ION			
6.0		3397.0	234970.0	NITRIC OXIDE ION			
2.0				30.007	2.880		NO+
5	8	0.0		OXYGENION			
4.0		26808.0		OXYGENION			
6.0		26829.0		OXYGENION			
4.0		40467.0		OXYGENION			
4.0		40468.0		OXYGENION			
2.0		0.0	372900.0	OXYGENION	1.0		O+
1.0				NITROGEN ION			
6	9	0.0		NITROGEN ION			
1.0		49.0		NITROGEN ION			
3.0		131.0		NITROGEN ION			
5.0		15316.0		NITROGEN ION			
5.0		32687.0		NITROGEN ION			
1.0		47168.0		NITROGEN ION			
5.0		0.0	447700.0	NITROGEN ION	14.007	1.0	N+
1.0							
006010		0.0					O++
1.0		113.4					O++
3.0		306.8					O++
5.0		20271.0					O++
5.0		42183.5					O++
1.0		60312.1					O++
5.0		0.0	1183500.0		16.000	1.0	O++
1.0							N++
005011		0.0					N++
2.0		174.5					N++
4.0		57192.1					N++
2.0		57252.0					N++
4.0		57333.2					N++
6.0		0.0	1130500.0		14.007	1.0	N++
1.0		0.0			.21153	.78847	
0.		0.0			0.0		
0.		0.0			0.0		
0.							

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TABLE I.- COMPARISON OF RESULTS TO THOSE OF REFERENCE 2

TABLE 1.1.- COMPARISON OF RESULTS TO THOSE OF REFERENCE 2												
(a) Dimensionless enthalpy H/RT ; $RT = 2.88105E+6T$ ergs/gm, $P_0 = 0.12882E-2$ gm/cm ³				(b) Dimensionless entropy S/R ; $R = 2.88105E+6$ ergs/gm °K				(c) Pressure; $P_0 = 1.01325E+6$ dynes/cm ²				
$T, ^\circ K$	References 2 and 3	Present report	Error	Relative error	References 2 and 3	Present report	Error	Relative error	References 2 and 3	Present report	Error	Relative error
$P/P_0 = 10^2$												
2,000	3.9694	3.9630 (A)	0.0064	0.0016	24.6859	24.6611 (A)	0.0248	0.0010	7.3248E+2	7.3258E+2 (A)	0.0010E-2	0.0001
4,000	4.613 ^b	4.5753 (A)	0.0377	0.0082	27.593 ^b	27.5039 (A)	0.0791	0.0029	1.4753E+3	1.4766E+3 (A)	0.0007E-3	0.0005
6,000	5.286 ^b	5.2446 (A)	0.0354	0.0067	29.788 ^b	29.6867 (A)	0.1013	0.0034	2.3244E+3	2.3317E+3 (A)	0.0073E-3	0.0031
8,000	5.8374	5.8229 (A)	0.0145	0.0025	31.5380	31.4611 (A)	0.0769	0.0024	3.3307E+3	3.3307E+3 (A)	0.0214E-3	0.0065
10,000	6.7300	6.7253 (A)	0.0047	0.0007	33.4635	33.3816 (A)	0.0819	0.0024	4.4968E+3	4.5444E+3 (A)	0.0476E-3	0.016
12,000	8.0548	8.1073 (A)	-0.0525	-0.0065	35.7469	35.7092 (A)	0.0377	0.0010	6.0414E+3	6.1482E+3 (B)	1.068E-3	0.177
15,000	9.9741	10.1130 (A)	-1.1389	-0.0139	39.0946	39.1350 (A)	-0.0404	-0.0010	8.9572E+3	9.1482E+3 (A)	1.068E-3	0.177
									9.1598E+3	9.1996E+3 (B)	2.426E-3	0.0271
									9.1996E+3	9.1996E+3 (A)	2.426E-3	0.0271
$P/P_0 = 10^{-7}$												
2,000	7.5346	7.5761 (A)	-0.0415	-0.0055	49.1448	49.1696 (A)	-0.0248	-0.0005	8.1807E-7	8.1904E-7 (A)	0.0097E-7	0.0012
4,000	20.0394	20.1906 (A)	-0.1512	-0.0075	67.2446	67.4095 (A)	-0.1649	-0.0025	2.4043E-6	2.4122E-6 (A)	0.0079E-6	0.0033
6,000	23.4574	23.6476 (A)	-0.1902	-0.0081	79.4494	79.7313 (A)	-0.2819	-0.0035	4.4810E-6	4.5003E-6 (A)	0.193E-6	0.0043
8,000	45.8267	46.0553 (A)	-0.2286	-0.0050	108.7672	109.1373 (A)	-0.3701	-0.0034	9.3403E-6	9.3758E-6 (A)	0.0355E-6	0.0038
10,000	53.0392	53.3278 (A)	-0.2886	-0.0054	126.2024	126.6830 (A)	-0.4806	-0.0038	1.4494E-5	1.4558E-5 (A)	0.0064E-5	0.0044
12,000	46.4030	46.6381 (A)	-0.2351	-0.0051	127.8812	128.3695 (B)	-0.4883	-0.0038	1.7500E-5	1.7578E-5 (B)	0.0078E-5	0.0045
15,000	43.1860	43.2423 (B)	-0.0563	-0.0013	133.3244	133.3660 (A)	-0.0437	-0.0025	2.2719E-5	2.2782E-5 (B)	0.0063E-5	0.0028
		39.5318 (A)	3.6542	0.0846		129.9422 (A)	-3.3822	-0.0254		2.1977E-5 (A)	-0.0742E-5	-0.0327

^aLetters in () indicate gas model.

^bIndicates values obtained from reference 3 since no value was given in reference 2.

TABLE II.- COMPARISON OF RESULTS TO THOSE OF REFERENCE 1

TABLE III. - COMPARISON OF RESULTS TO MODES OF REFERENCES I												
(a) Dimensionless Enthalpy H/RT ; $RT = 2.88105E+6T$ ergs/gm				(b) Dimensionless Entropy S/R ; $RT = 2.88105E+6T$ ergs/gm °K				(c) Pressure; $P_0 = 1.01325E+6$ dynes/cm ²				
$T, ^\circ K$	$P/P_0 = 10$			Relative error	$P/P_0 = 10$			Relative error	$P/P_0 = 10$			Relative error
	Reference 1	Present report	Error		Reference 1	Present report	Error		Reference 1	Present report	Error	
8,000	6.933	6.955 (B) 6.954 (A)	-0.022 -.021	-0.0032 -0.0030	3.522E+1 3.522E+1 (A)	3.522E+1 (B) 4.240E+1 (B)	0 0	0 0	3.631E+2 3.645E+2 (A)	3.645E+2 (B) 7.591E+2 (A)	0.014 -.014	0.0038 .0038
12,000	11.391	11.544 (B) 11.543 (A)	-0.153 -.152	-0.0134 -0.0133	4.250E+1 4.240E+1 (A)	4.240E+1 (B) 4.764E+1 (B)	0.010E+1 0.008E+1	0.0024 0.0017	7.506E+2 7.591E+2 (A)	7.591E+2 (B) 1.370E+3 (B)	0.085 0.010	0.0113 0.0074
18,000	12.933	12.825 (B) 12.825 (A)	0.108 0.108	0.0084 0.0084	4.772E+1 4.764E+1 (A)	4.764E+1 (B) 5.129E+1 (B)	0.008E+1 0.071E+1	0.0017 0.0137	1.360E+3 2.041E+3	1.370E+3 (A) 2.065E+3 (B)	0.010 0.024	0.0074 0.0117
24,000	14.222	13.806 (B) 13.606 (A)	0.416 0.616	0.0433 0.0433	5.199E+1	5.129E+1 (A)	0.071E+1	0.0137	2.041E+3	2.065E+3 (A)	0.024	0.0117
$P/P_0 = 10^{-6}$												
8,000	29.911	30.237 (B) 30.237 (A)	-0.326 -.326	-0.0109 -0.0109	8.704E+1	8.748E+1 (B) 8.748E+1 (A)	-0.044 -.044	-0.0051 -.0051	7.328E-5	7.376E-5 (B) 7.376E-5 (A)	0.048E-5 0.048E-5	0.0066 0.0066
12,000	46.218	46.453 (B) 46.450 (A)	-0.235 -.232	-0.0051 -0.0050	1.185E+2	1.190E+2 (B) 1.190E+2 (A)	-.005 -.005	-.0042 -.0042	1.744E-4	1.752E-4 (B) 1.752E-4 (A)	0.008E-4 0.008E-4	0.0046 0.0046
18,000	46.410	46.473 (B) 34.783 (A)	-.063 11.627	-.0014 2.905	1.336E+2	1.339E+2 (B) 1.220E+2 (A)	-.003 0.116	-.0022 0.0863	2.987E-4	2.995E-4 (B) 2.57E-4 (A)	0.008E-4 -.350E-4	0.0027 -.1172
24,000	62.361	62.229 (B) 28.923 (A)	0.132 33.538	0.0021 0.5378	1.633E+2	1.635E+2 (B) 1.240E+2 (A)	-.002 -.393	-.0012 0.2407	5.214E-4	5.220E-4 (B) 3.516E-4 (A)	0.006E-4 1.698E-4	0.0012 -.3257

^aLetters in () indicate gas model.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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